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Project Summary ORIGINAL

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Analysis of SOCMI VOC Fugitive Emissions Data

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The report gives results of an examination of fugitive emissions data from Synthetic Organic Chemical Manufacturing Industry (SOCMI) processing units (collected under earlier EPA studies) for correlations between process variables and leak frequency. Although line temperature did not have a consistent relationship with leak frequency, the data showed that leak frequency increased with increasing line pressure. Also, emissions factors for three process types (vinyl acetate, cumene, and ethylene) were developed and presented. Increases in mass emissions due to occurrence and recurrence of leaks for these three process types are also estimated. Finally, the effect of adjusting portable hydrocarbon readings by chemical response factor curves on leakage frequency estimates is investigated. Despite the wide range of response factors encountered, the adjusted leak frequencies were essentially the same as the unadjusted frequencies.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The contribution of fugitive leaks from process unit components are being investigated as a potential source of Volatile Organic Compound (VOC) emissions in the Synthetic Organic Chemical Manufacturing Industry (SOCMI). The purpose of this study was to provide an in-depth analysis of data on emissions collected under EPA contracts 68-02-3171-1, 68-02-3173-2 and -11, 68-02-3174-5, and 68-02-3176-1 and -6, and 68-03-2776-4. These data were collected by Radian, PEDCo, TRW, and Acurex and are summarized in EPA reports EPA-600/2-81-003 (NTIS PB 81-141566) and 600/2-81-080 (NTIS PB 81-206005). The results of this study will be available for use in evaluating VOC fugitive emissions.

The study design and test procedures for the data analyzed in this report are described in the above-mentioned EPA reports. The 24 process units studied in the data collection programs were selected to represent a cross-section of the population of the SOCMI. Several factors were considered during process unit selection, including total annual production in volume, number of producers, process conditions, corrosivity, volatility, toxicity, and value of the final chemical product. Factors varied widely from unit type to unit type, so that the selected process unit types represented a reasonable sample of the variety of chemical process units encountered in SOCMI.

The leak frequency in SOCMI was evaluated by the collection of screening data from 24 process units, where a screening value is the maximum repeatable concentration of total hydrocarbons detected at a source with a portable hydrocarbon detector. Maintenance was evaluated by measurement of fugitive emission leak rates (lb/hr) at

selected sources before and after maintenance at six process units representing three chemical processes. The results of these two programs provide the background necessary for the current study:

- Source population data.
- Screening value profiles for each source type.
- Screening-to-emission rate relationships.

The screening procedures began with the definition of the process unit boundaries. All feed streams, reaction/separation facilities, and product and by-product delivery lines were identified on process flow diagrams and in the process unit. Process data, including stream compositions, line temperatures, and line pressures, were obtained for all flow streams.

The Century Systems Models OVA-108 and OVA-128 hydrocarbon detectors were used for screening. The detector probe of the instrument was placed directly on those areas of the sources where leakage would typically occur. For example, gate valves were screened along the circumference of the annular area around the valve stem where the stem exits the packing gland and at the packing-gland/valve-bonnet interface. The actual leak rates were measured using a flow-through method described in report EPA-600/2-80-075a (NTIS PB 80-225253), and were analyzed on Byron Total Hydrocarbon Analyzer.

All accessible sources of the following source types were screened:

- Process valves.
- Pump seals.
- Compressor seals.
- Agitator seals.
- Relief valves.
- Process drains.
- Open-ended lines.

Also, a randomly selected subset of flanges were screened. Originally, only 5 percent of all flanges were screened. The subset was increased to 20 percent of all flanges when initial results indicated a higher frequency of emitting flanges than had been encountered in previous programs. The important variables available from this study are: screening value, source category, stream service, source type, chemical produced, ambient temperature elevation, line temperature, and line pressure. For the purposes of this report, a source is defined as "leaking" if its screening value is greater than or equal to 10,000 ppmv.

This summary presents conclusions based on four distinct data analysis tasks: 1) an analysis of important correlating process parameters (line pressure, etc.); 2) emission factor development for three specific chemical processes (seven units); 3) an evaluation of the increase in mass emissions due to occurrence and recurrence of leaks; and 4) an analysis of the impact on leak frequency from adjusting screening values by VOC detector response factors.

Conclusions

1) Relationship of Leak Frequency to Process Parameters

The process parameters that were examined for their effect on leak frequency were: process, service, material in the line, line pressure, line temperature, ambient temperature, and source elevation. Data on four source types (valves, pump seals, flanges, and open-ended lines) were used to examine the effects of these parameters. The sources were grouped into 32 categories based on source type, process type, stream service, and primary chemical in the line. These groupings were for statistical reasons and were not based on engineering reasoning.

Stream service was defined as gas, light liquid, or heavy liquid. Heavy liquids were not included in any analyses, since they leaked so rarely regardless of the other conditions. Gas stream service generally had a higher leak frequency than light liquid service. Proceeding with four source types and two stream service types, the data were then categorized by process unit as ethylene processes, high leaking processes, or low leaking processes. The ethylene units were analyzed separately because of the large number of sources in ethylene processes and their high leak frequency. The high leaking group consisted of all other units with greater than 1 percent of all source types leaking. The low leaking group consisted of all units with less than 1 percent of all source types leaking. Since very few sources leaked, the low leaking process units were not considered in further analyses. Within these process unit groups, the data were further subdivided by primary materials in the line. Caution should be used in these evaluations, however, since other chemicals in the line may also have an effect on leak frequency.

Examination of the data within these categories resulted in the following conclusions for this data set:

- Leak frequency was affected not only by the type of chemical process but also by the type of primary material in the line.
- Control valves had a higher leak frequency than block valves.
- For block valves, gate valves had a higher leak frequency than most of the other types, and plug and ball valves had lower leak frequencies.
- On-line pump seals had an overall leak frequency of 13.1 percent versus 4.9 percent for off-line pump seals.
- These data did not show a difference in leak frequency between double and single mechanical pump seals, although the type of barrier fluid was unknown and therefore unaccounted for in this analysis.
- Line pressure was seen to have a statistically significant effect in almost every case, with higher levels of pressure associated with higher leak frequencies.
- Line temperature had no consistent effect on leak frequency. The combined effect of line pressure and temperature was important in some cases.
- Ambient temperature had a consistent effect on leak frequency; however, the effect was not statistically significant for a majority of the cases. Higher leak frequencies tended to be associated with the higher ambient temperature category.
- Elevation had no consistent effect on leak frequencies. In the four cases where a statistically significant effect was observed, sources at ground level had a higher leak frequency than sources at higher elevations.

2) Emission Factor Development

The sources included in the development of the emissions factors are all valves and pump seals screened in the seven ethylene, cumene, and vinyl acetate process units, or 51.2 percent (16,575) of all valves and pump seals screened in the screening program. Since leak rate screening value models were only developed for these three process types, emissions factor estimation was limited to these three processes.

The emissions factors developed in this study are reported in Table 1. The

Table 1 *Estimated Emission Factors for Nonmethane Hydrocarbons from Valves and Pump Seals*

Source Type	Emissions Factor (95% Confidence Interval) (lb/hr)	(kg/hr)
Valves		
— Gas Service		
Ethylene processes	*0.024(0.008, 0.07)*	*0.011(0.004, 0.03)*
Cumene processes	*0.011(0.003, 0.05)*	*0.0052(0.001, 0.02)*
Vinyl acetate processes	*0.0046(0.001, 0.03)*	*0.0021(0.0004, 0.01)*
— Light Liquid		
Ethylene processes	*0.020(0.007, 0.06)*	*0.010(0.003, 0.03)*
Cumene processes	*0.0056(0.002, 0.02)*	*0.0025(0.001, 0.01)*
Vinyl acetate processes	*0.0003(0.0001, 0.002)*	*0.0001(0.00003, 0.001)*
Pump Seals		
— Light Liquid		
Ethylene processes	*0.069(0.006, 0.8)*	*0.031(0.003, 0.4)*
Cumene processes	*0.052(0.001, 2.7)*	*0.023(0.0004, 1.2)*
Vinyl acetate processes	*0.0043(0.0001, 0.1)*	*0.0020(0.00006, 0.06)*

emissions factors for the ethylene process are consistently higher than the factors for the cumene and vinyl acetate processes. The vinyl acetate process tends to have the lowest emissions factors of the three process types.

Cumulative distributions of screening values and mass emissions as a function of screening values were also developed for each of the three processes. Table 2 gives the estimates and confidence intervals from these curves for a 10,000 ppmv screening value.

3) Increase in Mass Emissions Due to Occurrence and Recurrence

Data collected during the EPA SOCMI maintenance program were further analyzed to estimate the effects of leak occurrence and recurrence on mass emissions. The following conclusions are based on these analyses:

- The increase in emissions for valves for which a leak occurred over a 1 to 6 month period was estimated to be 530 percent (95 percent confidence interval of 200 to 900 percent).
- Not enough data was available to accurately quantify the effect on emissions from leak occurrence from pump seals. However, the percent increase estimate was 75 percent with a 95 percent confidence interval of -100 to 6000 percent.
- The percent increase in emissions for valves with a leak recurrence within the 6 month period was estimated to be 510 percent (95 percent confidence interval of -100 to 1700 percent).
- Further analysis of the effect of valve maintenance on emissions showed a 98 percent reduction in emissions for valves which were "repaired" (screening value <10,000 ppmv after maintenance) and a 63 percent reduction for sources which were "not repaired" (screening value remained ≥10,000 ppmv after simple, on-line maintenance).

4) Impact of Response Adjustments on Leak Frequency Estimation

Three different techniques were used to adjust the original screening value for each source:

Table 2. *Summary of Percent of Sources Distribution Curves and Percent of Mass Emissions Curves at Screening Value of 10,000 PPMV*

Source Type	Percent of Sources Screening ≥10,000 ppmv: Estimate	95% Confidence Interval	Percent of Mass Emissions Attributable to Sources Screening ≥10,000 ppmv: Estimate	95% Confidence Interval
Valves				
Gas				
Ethylene	*15*	*(14, 16)*	*94*	*(93, 95)*
Cumene	*16*	*(13, 19)*	*94*	*(90, 96)*
Vinyl acetate	*3.7*	*(2, 5)*	*90*	*(85, 94)*
Light Liquid				
Ethylene	*26*	*(24, 27)*	*89*	*(87, 90)*
Cumene	*12*	*(10, 13)*	*80*	*(72, 86)*
Vinyl acetate	*0.2*	*(0, 0.4)*	*25*	*(9, 47)*
Pump Seals				
Light Liquid				
Ethylene	*30*	*(20, 39)*	*96*	*(90, 98)*
Cumene	*14*	*(1, 27)*	*89*	*(50, 98)*
Vinyl acetate	*1.7*	*(0, 4)*	*67*	*(5, 92)*

- The original OVA reading adjusted for the associated OVA response relationship of the primary chemical compound in the line.
- Weighted logarithmic average of response of primary and secondary chemicals.
- Weighted arithmetic average of response of primary and secondary chemicals.

The percent of leaking valves was calculated for each of the three estimates for both gas and light liquid services. The three estimates were found to be similar in most cases to the leak frequency based on the original screening values. Table 3 presents the overall results.

Table 3. Comparable Estimates for Percent Leaking (Valves) (24 SOCMI Process Units)

Process Stream	Number Screened[a]	Percent Leaking Based on OVA Readings	Percent Leaking Based on Method 1 Adjustments[b]	Percent Leaking Based on Method 2 Adjustments[c]	Percent Leaking Based on Method 3 Adjustments[d]
Gas	9,374	11.3	10.1	10.2	10.3
Light Liquid	18,133	6.1	5.3	5.6	5.5

[a] *119 sources with screening values = 10,001 ppmv were excluded.*
[b] *Method 1 is the adjustment to the OVA reading based on the response of the primary chemical in the line.*
[c] *Method 2 is the mixed chemical weighted logarithmic average technique.*
[d] *Method 3 is the mixed chemical weighted average technique.*

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The complete report, entitled "Analysis of SOCMI VOC Fugitive Emissions Data," (Order No. PB 81-234 270; Cost: $18.50, subject to change) will be available only from:
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